

Modified

G R O

Method for Determining Gasoline Range Organics

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MODIFIED METHOD FOR DETERMINATION OF GASOLINE RANGE ORGANICS

1. Scope and Application

- 1.1 This method is designed to measure the concentration of gasoline range organics in water and soil. This corresponds to a hydrocarbon range of C₆ - C₁₀ and a boiling point range between approximately 60°C and 220°C. As defined in the method, other organic compounds, including chlorinated solvents, ketones, ethers, mineral spirits, stoddard solvents, and naphthas are measurable. GRO results include these compounds/products.
- 1.2 The Limit of Quantitation (LOQ) of this method for gasoline range organics is 10 mg/kg or less for soils and 0.1 mg/L or less for groundwater.
- 1.3 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use.
- 1.4 **This method can be used to determine GRO and petroleum volatile organic compounds (PVOCs) concurrently.** Section 9.4 contains requirements for analyzing GRO and PVOCs concurrently.

2. Summary of Method

- 2.1 This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline, stoddard solvent, or mineral spirits. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on FID detector response to a gasoline component standard.
- 2.2 This method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is then analyzed by purge-and-trap GC.
- 2.3 Soil core samples are collected in wide mouth VOC vials and preserved with methanol. Minimum handling is required to reduce loss of contaminants.
- 2.4 This method is based in part on 1) USEPA SW-846: Methods 5030, 8000, 8020, 8015; 2) a single laboratory method evaluation study conducted by the American

Petroleum Institute; 3) work by the EPA Total Petroleum Hydrocarbons Committee; and 4) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

3. Definitions

- 3.1 Gasoline Range Organics (GRO): All the chromatographic response falling between the onset of the methyl-tertiary-butyl ether peak and the conclusion of the naphthalene peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Gasoline Component Standard.
- 3.2 Gasoline Component Standard: A ten component blend of typical gasoline compounds (Table 4). This standard serves as a quantitation standard and is used to establish a retention time window for gasoline range organics.
- 3.3 Laboratory Control Spike - Water: A reagent water spiked with the Gasoline Component Standard and run through the method with water samples as a quality control check. See Section 10.3.1.
- 3.4 Laboratory Control Spike - Soil: A reagent sand or clean soil sample spiked with the Gasoline Component Standard and run through the method with soil samples as a quality control check. See Section 10.3.2.
- 3.5 Method Blank - Water: A reagent water sample, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.3 for method blank acceptance criteria.
- 3.6 Method Blank - Soil: A reagent sand or clean soil extracted with the same volume of methanol used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.4 for method blank acceptance criteria.
- 3.7 Calibration Check Standard (CCS): A calibration standard analyzed to verify the validity of the calibration curve. See section 10.3.5 for CCS acceptance criteria.
- 3.8 Temperature Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper cooling of samples has been achieved. A 40 ml or 60 ml vial will be adequate for this purpose.
- 3.9 Methanol Trip Blank: A reagent methanol sample that accompanies samples in shipping and is transferred to a clean sample collection vial in the same manner as

samples are preserved with methanol. The transfer is made at some time during the sampling event and is used as a check on cross contamination of methanol preserved samples.

3.10 Other terms are as defined in SW-846.

4. Interferences

- 4.1 High levels of heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for GRO. Other organic compounds, including chlorinated solvents, ketones, and ethers are measurable. As defined in the method, the GRO results include these compounds. Spills of neat products should be quantified by specific analysis for the product in question. An example of a neat product would be a spill of (or storage tank containing) benzene.
- 4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol for preservation. Trip blanks prepared from both reagent water and methanol must be carried through sampling and subsequent storage and handling to serve as a check on such contamination.
- 4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in a oven at or above 105°C between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. **A screening step is recommended to protect analytical instrumentation.** Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination. Contamination limits for blanks can be found in sections 10.3.3 and 10.3.4.
- 4.4 The retention time window definition (methyl-tertiary-butyl ether to naphthalene) introduces a negative bias of approximately 25%. This bias may be greater for weathered samples particularly, low level samples. Laboratories are required to report peaks detected outside the window so contamination outside the window is not missed. Use of a standardized window improves comparability between

laboratory data. Note that gasoline blends often contain 10% ethanol which could be responsible for a portion of this negative bias.

5. Safety Issues

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6. Apparatus and Materials

6.1 Gas Chromatograph

- 6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases and syringes. A data system capable of determining peak areas and integrating GRO as defined in the method is required.

6.1.2 Columns:

- 6.1.2.1 Column 1: 105 M x 0.53 mm I.D. Restek RTX 502.2 3 micron film thickness, or equivalent.
- 6.1.2.2 Other columns such as a 30 M x 0.53 mm DB-5 may be used. Capillary columns are required to achieve the necessary resolution. The column must be capable of resolving typical gasoline components. It must also resolve methyl-tertiary-butylether (MTBE) from the methanol solvent front and ethylbenzene from m/p-xylene. Some columns may require subambient cooling to achieve these criteria.
- 6.1.3 Detector: Flame ionization (FID), or FID in series with a Photoionization detector (PID) if GRO/PVOCs are being determined concurrently.

- 6.1.4 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.
- 6.1.4.1 The required purging chamber is designed to accept 5 ml samples with a water column at least 3 cm deep. Purging volumes larger than 5 mls must not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.
- 6.1.4.2 The recommended trap is the Tekmar #8 trap (carbosieve/carbopack B). This trap is particularly good if problems are encountered with stability of MTBE. Alternatively, a trap of 25 cm long with an inside diameter of at least 0.105 in., containing the following packing can be used: 1) 1/3 of 2,6-diphenylene oxide polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent); 2) 1/3 of silica gel, 35/60 mesh, Davison grade 15 or equivalent; and 3) 1/3 of coconut charcoal, prepare from Barnebey Cheney, CA-580-26 log #M-2649, by crushing through 26 mesh screen. It is recommended that 1.0 cm of methyl silicone-coated packing, (3% OV-1 on chromosorb-W, 60/80 mesh or equivalent), be inserted at the inlet to extend the life of the trap. Another alternate trap uses 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat# 2-0321M). Other traps may be used. The Trap length and packing materials may be varied as long as equivalent performance has been verified.
- 6.1.4.3 Prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 ml/min. The trap may be conditioned at temperatures above 180°C if it is recommended by the manufacturer. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 180°C (or above) with backflushing. Traps other than the recommended should be desorbed according to the manufacturers guidelines. The trap may be vented to the

analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples.

6.1.4.4 The desorber should be capable of rapidly heating the trap to 180°C for desorption.

6.2 Analytical balance: A balance capable of accurately weighing 0.0001 g (must be used for standards). A top-loading balance capable of weighing to the nearest 0.1 g (should be used for sample analysis).

6.3 Ultrasonic bath.

6.4 VOC Vials: Wide mouth 40 ml (1.4 oz.), 60 ml (2.0 oz.), or 120 ml (4.0 oz.) VOC vials with teflon/silicone septa or teflon lined caps for soils and 40 ml (1.4 oz.) VOC vials with teflon/silicone septa for waters.

6.5 Syringes: 5 ml Luerlock glass hypodermic and a 5 ml gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Volumetric flasks: 10 ml, 50 ml, 100 ml, 500 ml, and 1,000 ml with a ground-glass stopper.

6.8 Microsyringes: 1 ul, 5 ul, 10 ul, 25 ul, 100 ul, 250 ul, 500 ul, and 1,000 ul.

6.9 Disposable pipets: Pasteur.

6.10 Spatula: Stainless steel.

7. Reagents and Standards

7.1 Reagent Water: GRO free water

7.2 Methanol: Purge and trap grade or equivalent. Store away from other solvents.

7.3 GRO free sand or soil

7.4 Individual Component Stock Standards: Volumetrically prepare stock standards for the gasoline components in methanol at approximately 20 mg/ml.

- 7.4.1 Place about 8 mls of methanol in a 10 ml tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.
- 7.4.2 Using a 500 ul syringe, immediately add 200-300 ul of the gasoline component to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.
- 7.4.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (ug/ul) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
- 7.4.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.
- 7.4.5 Standards must be replaced after six months unless comparison with unexpired standards documents their accuracy.
- 7.5 Gasoline Component Stock Standard: Commercially prepared gasoline component stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Gasoline Component Stock Standards can be prepared using individual component stock standard solutions. Prepare Gasoline Component Standard in methanol, as needed, at the concentrations shown in Table 4. These standards must be stored with minimal headspace and must be checked frequently for signs of degradation or evaporation.
- 7.6 Calibration Standards: Prepare Calibration standards at a minimum of five concentration levels in reagent water from the Gasoline Component Stock Standard. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC.

8. Sample Collection, Preservation, and Handling

- 8.1 Aqueous samples should be collected in triplicate (or the number of bottles directed by the laboratory) without agitation and without headspace in contaminant-free glass VOC vials with Teflon-lined septa in the caps. The Teflon liner must contact the sample. Samples must be preserved with 500 ul of 50% HCl at the time of collection, (acid must be added to the vial prior to adding the sample). Cool samples to 4°C immediately after collection. Water samples must be held at 4°C and analyzed within 14 days from the date of collection. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples preserved with sodium azide or extracted within 48 hours of collection.
- 8.2 Soil can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore™ sampler or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1. A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination (without methanol). A methanol trip blank must accompany each batch of samples (for each site and each day that samples are collected). See sections 3.9 and 10.4 for further instructions on methanol trip blanks. Care must be taken to be sure the vial seals properly (no soil on the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

Methanol preservation is mandatory for the Modified GRO method and must be noted on the chain of custody. Sample collection time must be verifiable from the chain of custody. Soil samples that arrive at the laboratory without methanol that have not been stored properly must be rejected. Flagging data for these samples will not be acceptable. (Proper storage is outlined in the Table 2.) Results from soil samples not preserved in methanol will be rejected. If the laboratory analyzes soil samples not handled as indicated in Table 2, at the request of clients, the samples must not be reported as "GRO".

- 8.2.1 Collect and preserve soil samples by one of the following techniques. Methanol preservation techniques can be found in section 8.2.2.

- 8.2.1.1 Collect soil into tared VOC vials following Table 1. Preserve immediately with methanol. Store samples on ice or at 4°C. Note that any samples collected in this fashion which are not analyzed by a laboratory are considered hazardous waste. Vials should be shipped in an upright position. Vials can also be placed in separate "ziplock" bags to avoid any problems that might occur if a vial leaks (such as the ink being removed from vial labels). Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.
- 8.2.1.2 Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with teflon sheets placed between the endcaps and the sample. Store samples on ice or at 4°C. Preserve with methanol within 2 hours of sample collection. Immediately prior to methanol preservation, the soil from the brass tube must be subsampled into a VOC vial following Table 1. Subsampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.
- 8.2.1.3 Pack soil with no headspace into an EnCore™ sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 4°C. Preserve with methanol within 48 hours of sample collection. Note that this allows the possibility of having the laboratory preserve the sample. If you intend to have the laboratory preserve the sample, it must be received at the laboratory within 40 hours of sample collection. Soil stored in the EnCore™ sampler must be extruded from the device into a VOC vial immediately prior to methanol preservation. The soil is extruded by using a pushrod supplied with the tool. Soil should not be scooped out of the sampler using a spatula, etc. EnCore™ samplers must be cleaned appropriately (following the manufacturers recommendations) prior to reuse.
- 8.2.1.4 Alternate sample storage devices equivalent or superior in performance to the brass tube or the EnCore™ sampler may be used for sample storage prior to methanol preservation. Alternate sample storage devices **must be approved** by the Department **prior to use**.

- 8.2.2 Methanol can be added by one of the methods listed below. Vials must not be submitted to the laboratory for analysis of any volatile parameter (GRO, PVOC, VOC) if any of the methanol has spilled in sampling. If the laboratory determines that a vial has leaked, by noting a visible reduction of volume, or an unusually low weight then this must be reported with analytical results. Only the vial that has leaked will be in question not the entire cooler or shipping package.
- 8.2.2.1 Samples collected directly into a VOC vial in the field can be placed into tared vials already containing the appropriate volume of methanol (see Table 1). Samples stored in the brass tube, EnCore™ sampler, or an approved alternate storage device, can be added to tared vials already containing the appropriate volume of methanol (see Table 1). Samples stored in the brass tube, EnCore™ sampler, or an approved alternate storage device, should be preserved after screening of collocated samples to determine which samples will be laboratory analyzed. Only those samples to be laboratory analyzed should be methanol preserved. Store samples on ice or at 4°C.
- 8.2.2.2 Methanol can be added from premeasured volumes provided by the laboratory or a commercial vendor. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, quickly open the soil vial and pour in the appropriate volume of methanol (see Table 1), closing the sample vial immediately. Store samples on ice or at 4°C. Unused vials of methanol may be used at other sites at the sampler's discretion. Professional judgement should be used in determining how long vials with methanol for preservation (or vials for trip blanks) can be stored. Labs may determine the shelf life for these vials if they wish to offer an exact time period for storage to their clients.
- 8.2.2.3 Premeasured volumes of methanol can be added via syringe from a septa vial provided by the laboratory or a private vendor containing the appropriate volume (see Table 1) or from bulk methanol in the laboratory. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, draw the appropriate volume of methanol into the syringe and add by puncturing the vial septa. Depending on the vial size and volume of methanol added,

venting of the vial may be necessary to facilitate adding the methanol. If necessary, vent the vial by partially unscrewing the vial top. A fresh syringe needle will be needed for each new vial to avoid cross contamination. Common laboratory glass syringes and noncoring type syringe needles should be used. Store samples on ice or at 4°C.

8.2.2.4 Methanol can be added using a teflon repeater pipet pump that attaches to a bottle of purge and trap grade methanol and delivers the appropriate volume of methanol (see Table 1). For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, quickly open the soil vial and depress the pipet pump to deliver the methanol, closing the sample vial immediately. If this method is used it is important to make sure that purge and trap grade methanol be used. Store samples on ice or at 4°C. Note that the methanol in the bottle can become contaminated if stored near any source of volatile fumes. Storage and use of this apparatus must be away from petroleum products and other volatile contaminants.

8.2.3 Shipping time should be minimized. Samples must be received by the lab within 4 days. Refer to Table 2 for soil sample holding times.

8.2.3.1 Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 to determine if the sample may be analyzed as is, requires addition of methanol, flagging, or must be rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, at the request of clients, the samples must not be reported as "GRO".

8.3 Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice". If samples are not "received on ice", temperature shall be determined from:

8.3.0.1 The temperature of an actual sample.

8.3.0.2 The temperature of a temperature blank shipped with samples.

8.3.0.3 The temperature of the melt water in the shipping container.

When no ice is in the cooler, no temperature blank is provided, and there is not sufficient sample volume to sacrifice for a temperature measurement, the laboratory must flag the sample result and state the condition of sample upon receipt (ie. not cooled during shipping, received at room temperature, etc.). **Note: If blue ice packs or similar methods are used, precooling of samples to 4°C with ice or by refrigeration is required.**

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap is used directly on groundwater samples. Soils and solids are analyzed by methanol extraction in the vial, followed by purge and trap. Soil concentrations must be reported on a dry weight basis. The procedure for determination of dry weight can be found in EPA method 5030, section 7.3.3.1.5.

NOTE: It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a solid sample's methanol extract (diluted), the headspace method (SW-846 method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820).

9.2 Gas Chromatography

9.2.1 Conditions for Column 1: Set helium column pressure as recommended by the manufacturer. Set column temperature to 40°C for 1 min, then 5°C/min to 100°C, then 8°C/min to 240°C and hold for 7.5 min. Conditions may be altered to improve resolution of gasoline range organics.

9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.2.

9.3 Retention Time Window and Quantitation

9.3.1 The retention time window is defined as beginning approximately 0.1 minutes before the onset of the methyl-tertiary-butylether peak and ending 0.1 minutes after the conclusion of the naphthalene peak in the calibration run.

- 9.3.2 Gasoline Range Organics (GRO): Quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Gasoline Component Standard. Further instructions on quantitation can be found in section 9.7.
 - 9.3.3 The laboratory must verify the placement of the retention time window at the beginning of each day and whenever a new GC column is installed or when significant retention time shifts occur. This can be accomplished as part of the calibration check.
 - 9.3.4 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. The correct baseline placement would a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 is intended to illustrate correct placement of the baseline for several situations.
- 9.4 The following instructions must be followed when using the PID in series with the FID for the optional determination of GRO and PVOCs concurrently.
- 9.4.1 PVOCs is an acronym for petroleum volatile organic compounds. Analysis for PVOCs is required at some LUST sites in lieu of VOC analysis. The compounds included in the PVOC list are all of the compounds in the GRO component standard except naphthalene. GRO/PVOCs may be determined from a single analysis by placing a PID in series with the FID required for GRO analysis.
 - 9.4.2 Extract soil samples as described in section 9.6.2. Following extraction, proceed with analysis procedures outlined in EPA SW-846 method 5030/8020 for the PVOC compounds (beginning at section 7.3.3.2.4 of method 5030A for methanol preserved soil samples). Capillary columns are required.
 - 9.4.3 The laboratory must perform an initial demonstration of capability to generate acceptable accuracy and precision (IDC) with EPA method 8020 as indicated in the method, with spike recoveries of 80%-120% and a relative standard deviation, (RSD)<20%.

- 9.4.4 Laboratories must achieve a limit of detection (LOD) of 25 ug/kg or lower for soil PVOCs. Lower detection limits are achievable for water samples. The Department will use 25 ug/kg as a reporting limit for soil PVOCs. A 25 ug/kg reporting limit means that laboratories need not report detection of PVOC compounds below 25 ug/kg (on a wet weight basis). The Department will not accept the use of reporting limits in lieu of actual LODs in other tests unless specified. The requirements for the LOD applies to all samples analyzed to meet the requirements of the NR 700 series. Sample results will not be used to establish clean closure if the laboratory LOD for PVOCs is higher than 25 ug/kg for any reason. If sample detection limits are elevated because of dilution (or other reasons) the Department will consider the sample concentrations to be above levels acceptable for site closure. The LOD must not be adjusted for the dry weight of the sample, however, sample results must still be reported on a dry weight basis. The reported LOD must be adjusted if the volume of sample extract purged is less than the amount used to determine the LOD.
- 9.4.5 PVOC soil samples having concentrations for any compound between the LOD and the LOQ when the clean-up criteria is below the LOD must be qualitatively confirmed by an alternate method to avoid false positive results. Effectively, confirmation is required for soil PVOCs between 25 ug/kg and 60 ug/kg when the clean-up criteria is below the LOD or has not been established (unless site specific criteria are available). See Table 5 for further examples of when confirmation is required. Confirmation is defined as analysis of the sample by a second column of a different phase or reanalysis using mass spectrometry (MS). Confirmation analyses must be performed with a methodology that has an LOD of 25 ug/kg or lower. Laboratories are not required to report compounds detected in the confirmation run that were not detected in the original run. Compounds that are not confirmed in the confirmation analysis will not result in additional clean-up at a site or hinder site closure.
- 9.4.6 Surrogates are mandatory for PVOC analysis. The internal standard quantitation method can be used but is not mandatory. Surrogates and internal standards must be chosen to avoid coelution with sample contaminants. A constant surrogate concentration, not to exceed 20 ug/l, must be maintained in all calibration standards, samples and blanks. No more than one surrogate and one internal standard can be used to avoid coelution interferences within the GRO window. Surrogates are added to samples and standards immediately prior to purging.

9.4.6.1 The minimum surrogate recovery is 80%. If surrogate recoveries are below 80% the problem must be corrected and samples whose results are in question must be rerun. No maximum surrogate recovery is specified because high recoveries will be assumed to be coelutions of sample.

9.4.7 The Gasoline Component Standard should be used to calibrate the PID for the optional concurrent determination of PVOCs. Remember, when calibrating, a constant concentration of surrogate (not to exceed 20 ug/l) must be added to all samples and all calibration standards. The response of the surrogate (and internal standard) will be included as part of the area used to generate the GRO calibration curve. [The laboratory may use an internal standard for quantitation of PVOCs but must not use it for quantitating GRO results.] Samples must be quantitated directly from the curve with no subtraction of surrogate (or internal standard) response. The inclusion of the surrogate within the calibration curve accounts for the surrogate added to the sample. Surrogate recovery must be assessed from the PID. If the internal standard area varies by more than a factor of two (-50% to +100%) from the last continuing calibration check, corrective action must be taken. When corrections are made, reanalysis of affected samples is necessary.

9.4.8 Because it will not be possible to perform the matrix spike/matrix spike duplicate required in method 8020 for methanol preserved soil samples, laboratories should substitute in their place, the LCS-soil and duplicate that are part of the required QC for the GRO method. Acceptable performance for the LCS-soil is 80%-120% recovery and a relative percent difference of, (RPD) $\pm 20\%$. Acceptable performance for LCS-water is 80%-120% recovery and RPD $\pm 20\%$.

9.4.9 Continuing calibration check standards must fall within $\pm 15\%$ of the corresponding curve response.

9.5 GRO Calibration:

9.5.1 Run the Gasoline Component Standard at a minimum of five concentration levels. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC. The recommended calibration range is 10-1000 ug/l. NOTE: Additional low points may be necessary for the optional PID quantitation.

- 9.5.2 Prepare final solutions containing required concentrations of calibration standards from the Gasoline Component Standard directly in the 5 ml glass syringe as follows:
1. Add the aliquot of calibration solution directly to the reagent water in the glass syringe by inserting the needle through the syringe end. A constant volume of methanol must be purged for both samples and standards
 2. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water.
 3. Attach the 2-way syringe valve to the syringe and then inject the standard into the purge vessel through the two way valve.
- 9.5.3 Inject 5 mls of each calibration standard utilizing the purge-and-trap analysis outlined in 9.6.1.9 - 9.6.1.12. Tabulate the entire area (baseline to baseline) for the ten components against the mass injected. Instructions for performing baseline to baseline integration can be found in section 9.7. The results are used to prepare a calibration curve by linear regression. The curve must have a correlation coefficient of at least 0.99.
- 9.5.4 Verify the working calibration curve at the beginning of each working day, by the injection of a Calibration Check Standard (CCS). If the concentration determined from the curve, for the CCS, varies from the known concentration by more than 20%, attempt to correct the problem. If a CCS, run after corrective action has been performed, varies by more than 20% from the known concentration, a new calibration curve must be prepared.
- 9.6 Gas Chromatography Analysis:
- 9.6.1 Water Samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method.
- 9.6.1.1 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 ml/min on the purge-and-trap device.
 - 9.6.1.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe plunger and compress the

sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one sample vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. If a second analysis is needed from a syringe, analysis must be performed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

- 9.6.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe. Sample dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.
- 9.6.1.4 Dilutions may be made in volumetric flasks (10 ml to 100 ml). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.
- 9.6.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.
- 9.6.1.6 Inject the proper aliquot of samples from the syringe as prepared in Paragraph 9.6.1.2 into the flask. Aliquots of less than 1 ml are not recommended. Dilute the sample to the mark with reagent water. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.
- 9.6.1.7 Fill a 5 ml syringe with diluted sample as in Paragraph 9.6.1.2.
- 9.6.1.8 Attach the two-way syringe valve to the syringe and inject sample into the purging chamber through the two-way valve.
- 9.6.1.9 Close both valves and purge the sample for 11.0 ± 0.1 min.

- 9.6.1.10 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C and backflushing the trap with inert gas between 15 and 20 ml/min for 4 minutes.
 - 9.6.1.11 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with minimum of two 5 ml flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.
 - 9.6.1.12 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher the temperature, the shorter the useful life of the trap. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.
 - 9.6.1.13 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, the laboratory must verify that carry-over did not occur. If carryover is found to have affected subsequent samples, the system must be decontaminated and the affected samples repurged.
- 9.6.2 Methanol Extraction for Soil/Sediment: This method is based on extracting the sediment/soil with methanol. An aliquot of the extract is added to reagent water and purged at the conditions indicated in Table 3. A screening analysis is recommended (see 9.1).
- 9.6.2.1 Extract samples weighed in section 8.2.3.1.
 - 9.6.2.2 Hand shake sample in its vial vigorously for 2 minutes. Sonicate for 20 minutes.

- 9.6.2.3 Allow sediment to settle until a layer of methanol is apparent.
- 9.6.2.4 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging. A constant volume of methanol must be purged for samples, standards and blanks. Sample screening data can be used to determine the volume of methanol extract to purge. Additional methanol may be necessary to assure that a constant volume of methanol is added to the reagent water for analysis. An appropriate dilution is one that keeps the response (both area and peak height) of major constituents in the upper half of the calibration range. If an initial dilution does not accomplish this then an intermediate dilution should be performed.
- 9.6.2.5 Remove the plunger from a 5.0 ml Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract. Add the appropriate volume of methanol extract (100 ul maximum).
- 9.6.2.6 Attach syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.
- 9.6.2.7 Proceed with the analysis as in 9.6.1.9-9.6.1.13. Analyze all reagent blanks and QC samples on the same instrument as that used for the samples.
- 9.6.2.8 If the responses exceed the calibration or linear range of the systems, use a smaller aliquot of methanol extract or dilute aqueous sample.

9.7 Calculations:

- 9.7.1 GRO Calibration: Quantitation of GRO is performed by the external standard method. The concentration of Gasoline Range Organics in the sample is determined from a summation of the total response within the range of the elution of methyl-tertiary-butylether and naphthalene, using the calibration curve. No area may be subtracted from the GRO retention time window in calculating GRO results.

- 9.7.1.1 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The correct baseline coincides with a horizontal line drawn through the lowest point in the chromatogram before the end of the window. The lowest point may be within the window, before the window, or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 illustrates correct placement of the baseline for several chromatograms.
- 9.7.1.2 Refer to Section 9.3, Retention Time Windows and Quantitation, for information on establishing the retention time window. From linear regression of calibration standard GC responses (R) against their known concentrations (C in ug/l) derive the following linear equation:

$$C = mR + b$$

Using the slope (m) and the intercept (b) from this equation the concentration of the sample can be calculated from the following equations:

Water samples

$$C_s = (mR_s + b)(D)$$

Soil Samples

$$C_s = [(mR_s + b)(D)(V_l)(K)] / [(V_p)(W)]$$

Where:

C_s = Concentration of sample in ug/l for waters and mg/kg on a dry weight basis for soils

m = slope of the calibration curve

R_s = GC response of sample in the GRO retention time window

b = intercept of calibration curve

D = dilution factor if water sample or soil extract was diluted

V_p = volume of soil extract purged (units must be the same as those used for V_t)

V_t = total volume of soil extract

$K = 5 \times 10^{-6}$ l mg/ug (this constant adjusts for both conversion from ug/kg to mg/kg and for the dilution of the volume of extract purged up to the 5 mls used for purging)

W = total dry weight of soil sample in kg

- 9.7.2 Peak areas measured from blanks may not be subtracted from sample peak areas. All blank concentrations (above the LOD) must be reported. Sections 10.3.3 and 10.3.4 give acceptance criteria for blanks. Blank concentrations up to and including the acceptance criteria must be reported. Blank concentrations exceeding the acceptance criteria require reanalysis.
- 9.7.3 Report the presence of significant peaks outside the chromatographic window. Significant peaks are peaks which can be distinguished above the noise in a chromatogram. Any peak 3 times the standard deviation of the signal to noise ratio is statistically significant. To insure that peaks outside the GRO window are not missed, run the chromatogram out 5 minutes past the last component in the GRO component standard. All peaks (and baseline rises) outside the window are to be reported. If area outside the window is detected it must not be quantitated as part of the GRO result. Laboratories may quantitate this area outside the window against the GRO standard and report a concentration detected outside the window or simply report that peaks or baseline rises were detected outside the window.

10. Quality Control

- 10.1 The analyst must make an initial demonstration of the capability to generate acceptable accuracy and precision with this method by successful analysis of the following:
- 10.1.1 Replicate Laboratory Control Spike - Water: Analysis of 5 replicates at a concentration of 100 ug/l. Recoveries must fall between 80%-120% of the known concentration and the RSD must be <20%.
- 10.1.2 Replicate Laboratory Control Spike - Soil: Analysis of 5 replicates at a concentration of 10 mg/kg. Recoveries must fall between 75%-120% of the known concentration and the RSD must be <20%.
- 10.2 The laboratory must determine its LOD and LOQ for both soils and waters. The LOD determination must be performed in accordance with 40 CFR, Part 136, Appendix B. Soil LODs are performed in accordance with 40 CFR, Part 136, Appendix B using a GRO free sand or soil, and the same extraction method used for soil samples. The LOQ calculation can be found in "Principles of Environmental Analysis", Analytical Chemistry, Vol. 55, No. 14, December 1983, 2210-2218. The LOQ is defined as:

$$LOQ = 10(S)$$

Where S is the standard deviation determined from analysis of seven replicate spikes analyzed to determine the LOD in accordance with 40 CFR, Part 136, Appendix B.

- 10.3 With every batch of 20 samples or less the lab must analyze:

- 10.3.1 Duplicate Laboratory Control Spike - Water : The Duplicate LCS-water must be processed through the method in the same manner as water samples. The recovery of LCS-water spikes must be between 80%-120% and the RPD<20%. The LCS-water must be run with every batch of 20 water samples. One of the LCS-waters must be run at the beginning of a batch of samples and the other at the end. One of the LCS - waters may qualify as a replacement for the CCS.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS

run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

- 10.3.2 Duplicate Laboratory Control Spike - Soil : The Duplicate LCS-soil must be processed through the method in the same manner as soil samples. The recovery of the LCS-soil spikes must be between 80%-120% of the known concentration and the RPD<20%. The LCS-soil must be run with every batch of 20 soil samples. One of the LCS-soils must be run at the beginning of a batch of samples and the other at the end.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

- 10.3.3 Method Blank - Water: The method blank - water must be processed through the method in the same manner as water samples. If the concentration exceeds 50 ug/l, all water samples associated with this blank (samples run since the last blank that was below 50 ug/l) must be rerun.

- 10.3.4 Method Blank - Soil: The method blank - soil must be processed through the method in the same manner as soil samples. If the concentration exceeds 5.0 mg/kg, all soil samples associated with this blank (samples run since the last blank that was below 5.0 mg/kg) must be rerun.

- 10.3.5 Calibration Check Standard (CCS): The CCS response must be within \pm 20% of the value predicted by the curve or a new curve must be generated. The CCS must not be used to update the curve or used in any other manner for quantitation.

- 10.4 Methanol Trip Blank: Report results of methanol trip blanks with soil sample results. Not required for samples preserved in the laboratory.

- 10.5 Water Trip Blank: As required for water samples in NR 716. Report results of trip blanks with water sample results.

- 10.6 The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99.

- 10.7 If any of the criteria above are not met, the problem must be corrected before further samples are analyzed. Any samples analyzed between the last QC samples

that meet the criteria and those that have fallen out must be rerun. If this is not possible, affected sample results must be flagged.

10.8 Methanol blanks should be run after soil samples suspected of being highly concentrated to prevent carryover.

10.9 Standard gasoline and other light end fuel mixtures are available commercially if the laboratory desires additional performance indicators.

11. Method Performance

11.1 The required Limit of Quantitation (LOQ) is 10 mg/kg or less for soils and 0.1 mg/l or less for waters. A chromatogram for a Gasoline Component Standard is shown in Figures 2 and 3.

12. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 5030, 8000, 8015, and the current edition of 8020.
2. American Petroleum Institute "Sampling and Analysis of Gasoline Range Organics and Soils", in preparation.
3. "Evaluation of Proposed Analytical Methods to Determine Total Petroleum Hydrocarbons in Soil and Groundwater" prepared by Midwest Research Institute for USEPA Office of Underground Storage Tanks, August 14, 1990.
4. ASTM "Standard Practice for Sampling Waste and Soils for Volatile Organics" Draft #1, 2/16/87.
5. Parr, J.L., G. Walters, and M. Hoffman, "Sampling and Analysis of Soils for Gasoline Range Organics" presented at First Annual West Coast Conference Hydrocarbon contaminated Soils and Groundwater, 2/21/90.
6. American Petroleum Institute "Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater, August 1985, API Publ. 4395.
7. "Leaking Underground Fuel Tank (LUFT) Field Manual", State Water Resources Control Board, State of California, Sacramento, CA, May 1988.
8. Fitzgerald, John "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure" in Petroleum Contaminated Soils, Vol. 2, 1989.
9. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations", Ground Water Monitoring Review, 1987.
10. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.
11. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, "Volatile Organic Analysis for a Soil, Sediment or Waste Sample" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.
12. Siegrist, R.L., and P.D. Jenssen, "Evaluation of Sampling Method Effects on volatile Organic Compound Measurements in Contaminated Soils", Environmental Science and Technology, Vol. 24, November 9, 1990.

Table 1
Weight Maxima

Vial Size	Target Sample Weight	Actual Sample Weight	Volume of Methanol	Action
40 mls (GRO only)	10 gms	<8 gms	10 mls	Flag
		8-11 gms	10 mls	None
		>11 gms<20 gms	10 mls	Add Methanol
		>20 gms	for any amount	Reject
60 mls	10 gms	<8 gms	10 mls	Flag
		8-11 gms	10 mls	None
		>11 gms<35 gms	10 mls	Add Methanol
	25 gms	<20 gms	25 mls	Flag
		20-26 gms	25 mls	None
		>26 gms<35 gms	25 mls	Add Methanol
		>35 gms	for any amount	Reject
120 mls	10 gms	<8 gms	10 mls	Flag
		8-11 gms	10 mls	None
		>11 gms<70 gms	10 mls	Add Methanol
	25 gms	<20 gms	25 mls	Flag
		20-26 gms	25 mls	None
		>26 gms<70 gms	25 mls	Add Methanol
	50 gms	<40 gms	50 mls	Flag
		40-51 gms	50 mls	None
		>51 gms<70 gms	50 mls	Add Methanol
		>70 gms	for any amount	Reject

Laboratories should use standard rounding rules to determine compliance with the maximum weight requirement. Sample weights should be rounded to the nearest whole number. This means that a sample weighing between 34.5-35.4 is rounded to 35.0 gms, and a sample weighing between 69.5-70.4 gms is rounded to 70.0 gms. There will be NO allowances given past these tolerances.

Table 2
Sample Holding Times and Storage

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		Solvent Addition	Shipping	Extraction	Analysis
GRO/VOC/PVOC soils	VOC vial	immediately	4 days	21 days	21 days
	Brass Tube	within 2 hours	4 days	21 days	21 days
	EnCore™	within 48 hours	40 hours	21 days	21 days
VOC/PVOC Confirmation soils	NA	NA	NA	NA	28 days
GRO/VOC/PVOC waters	VOC vial	NA	NA	14 days	14 days
GRO/VOC/PVOC carbonate aquifers	VOC vial	NA	2 days unless azide preserved	2 days unless azide preserved	14 days

Table 3
Purge and Trap Parameters

PURGE AND TRAP OPERATING PARAMETERS	
Purge gas	Nitrogen or Helium
Purge gas flow rate (ml/min)	40
Purge time (min)	11.0 ± .01
Purge temperature	Ambient
Desorb temperature (°C)	180
Backflush inert gas flow (ml/min)	20-60

Table 4

GASOLINE COMPONENT STANDARD AND CONCENTRATIONS	
Component	Concentration, ug/ml
Methyl-t-butylether	1000
Benzene	1000
Toluene	1000
Ethylbenzene	1000
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
1,3,5-Trimethylbenzene	1000
Naphthalene	1000
Total	10,000

Note: The concentration of the Gasoline Component Standard may be varied as long as the concentration of each component is the same.

Table 5

Confirmation Example			
Compound	Clean-up Criteria - NR 720 Table Values	Confirmation if results between	
Benzene	5.5 mg/kg	25 mg/kg	60 mg/kg
Ethylbenzene	2900 mg/kg	never	never
MTBE	ND	25 mg/kg	60 mg/kg
Toluene	1500 mg/kg	never	never
1,2,4-Trimethylbenzene	ND	25 mg/kg	60 mg/kg
1,3,5-Trimethylbenzene	ND	25 mg/kg	60 mg/kg
Xylenes, total	4100 mg/kg	never	never

Note that site specific clean-up criteria can be developed and would then supersede the table values. This table does not address compounds of interest other than the PVOCs.

Figure 1
Integration Examples

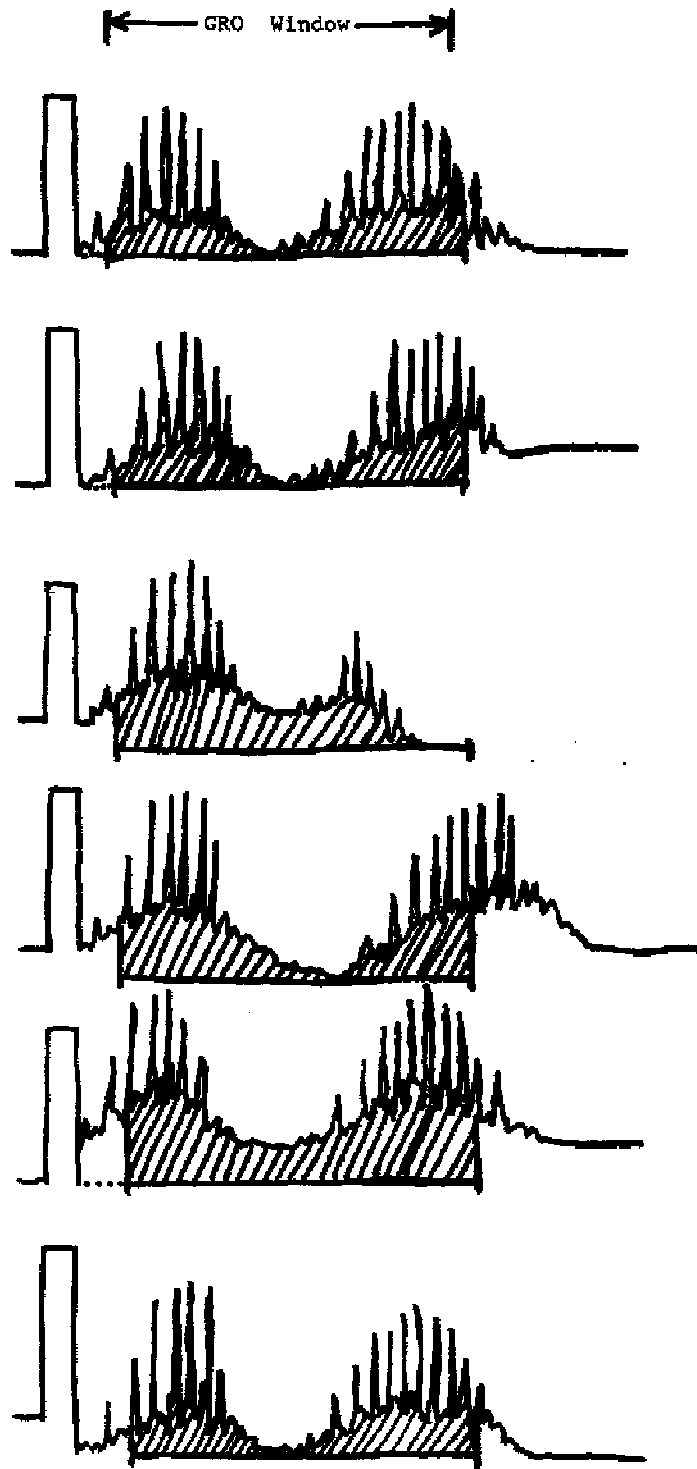


FIGURE 2
Gasoline Component Standard - FID

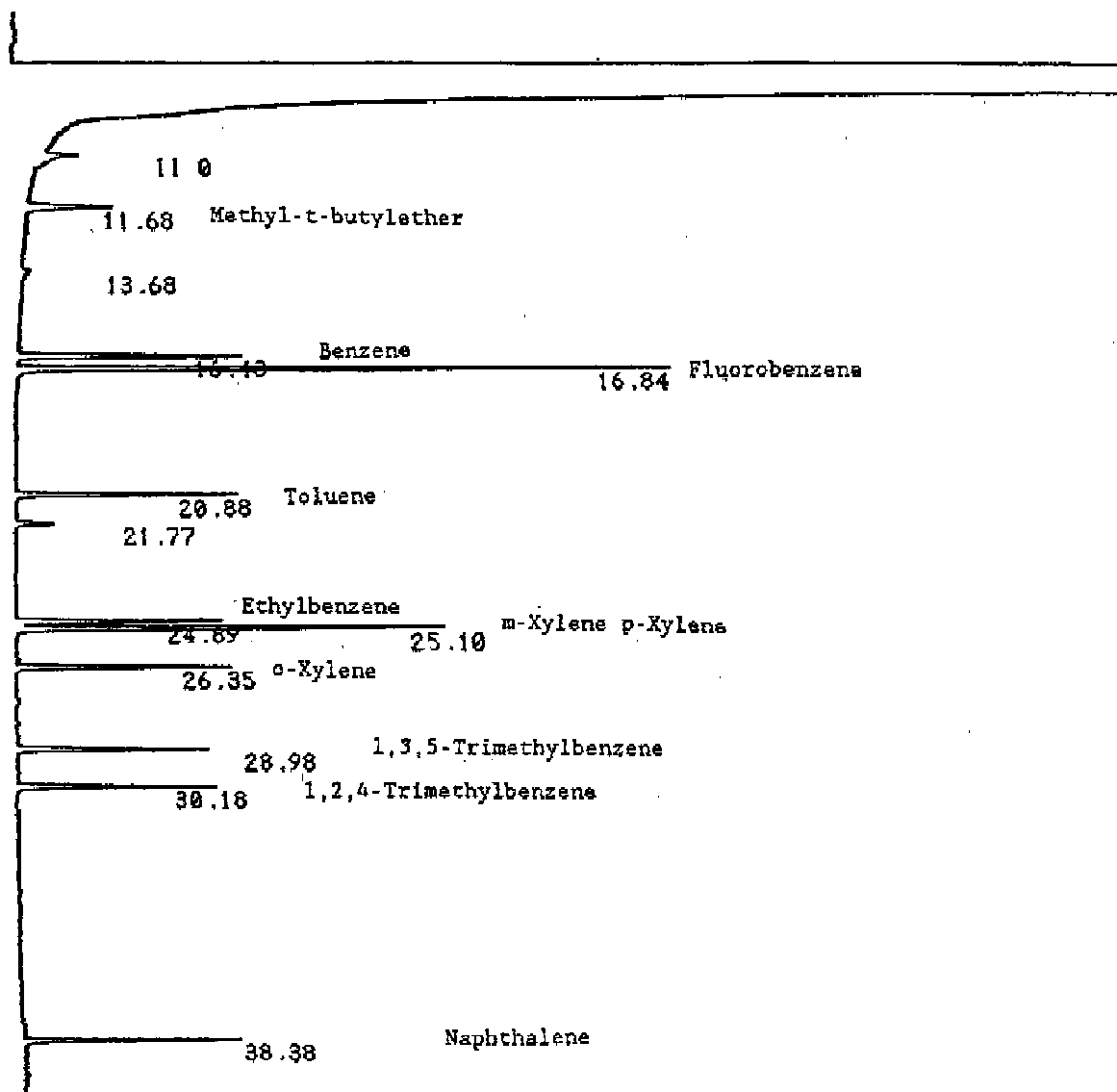
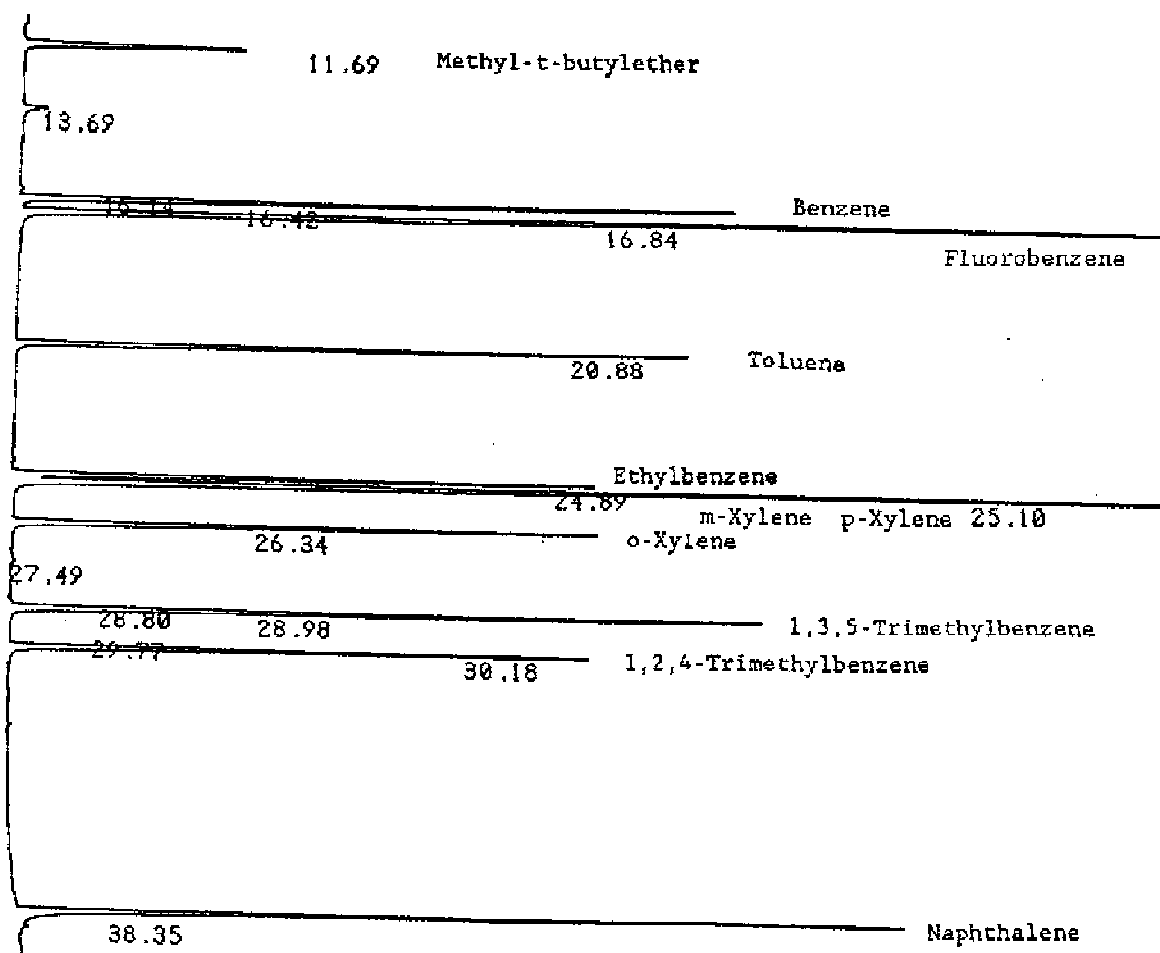


FIGURE 3
Gasoline Component Standard - PID



Modified

D R O

Method for Determining Diesel Range Organics

WISCONSIN DNR

September 1995

PUBL-SW-141

MODIFIED METHOD FOR DETERMINATION OF DIESEL RANGE ORGANICS

1. Scope and Application

- 1.1 This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a hydrocarbon range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C. As defined in the method, other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils are measurable. DRO results include these compounds/products.
- 1.2 The Limit of Quantitation (LOQ) of this method for diesel range organics is 10 mg/kg or less for soils and 0.1 mg/L or less for groundwater.
- 1.3 This method is based on a solvent extraction, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in solvent extraction and the use of gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use.
- 1.4 The method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional analyses may be necessary. These additional efforts are not contained within this method.

2. Summary of Method

- 2.1 This method provides gas chromatographic conditions for the detection of semivolatile petroleum fractions such as diesel, fuel oil #2, or kerosene. Samples are analyzed utilizing extraction to dissolve the organic constituents. The extract is dried, concentrated and injected into a capillary column gas chromatograph. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on FID detector response to a diesel component standard.
- 2.2 This method is suitable for the analysis of waters, soils, or wastes.
- 2.3 Soil core samples are collected in wide mouth VOC vials with minimum handling to reduce loss of contaminants. Preservation by solvent addition is performed in the lab.

- 2.4 This method is based in part on 1) USEPA SW-846: the 3rd edition of methods 8000 and 8100; 2) Method OA-2; 3) work by the EPA Total Petroleum Hydrocarbons Methods Committee; and 4) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

3. Definitions

- 3.1 Diesel Range Organics (DRO): All the chromatographic response falling between the onset of the n-decane (n-C₁₀) peak and the conclusion of the n-octacosane (n-C₂₈) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.
- 3.2 Diesel Component Standard: A ten component blend of typical diesel compounds (Table 3). This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics.
- 3.3 Laboratory Control Spike - Water: A reagent water spiked with the Diesel Component Standard and run through the method with water samples as a quality control check. See Section 10.3.1.
- 3.4 Laboratory Control Spike - Soil: A reagent sand or soil sample spiked with the Diesel Component Standard and run through the method with soil samples as a quality control check. See Section 10.3.2.
- 3.5 Method Blank - Water: A reagent water sample extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.3 for method blank acceptance criteria.
- 3.6 Method Blank - Soil: A reagent sand or clean soil extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.4 for method blank acceptance criteria.
- 3.7 Calibration Check Standard (CCS): A calibration standard analyzed to verify the validity of the calibration curve. See section 10.3.5 for CCS acceptance criteria.
- 3.8 Temperature Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper

cooling of samples has been achieved. A 40 ml or 60 ml vial will be adequate for this purpose.

3.9 Other terms are as defined in SW-846.

4. Interferences

- 4.1 Other organic compounds; including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the DRO results include these compounds. Spills of neat products should be quantified by specific analysis for the product in question. The definition of a neat product is a product containing only a single compound. An example of this would be a spill of (or storage tank containing) benzene.
- 4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water and extraction solvent. Method blanks must be analyzed with each batch or for every 20 samples to demonstrate that the analytical system is free of contamination. Contamination limits for blanks can be found in sections 10.3.3 and 10.3.4.
- 4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination.

5. Safety Issues

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6. Apparatus and Materials

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph and all required accessories, including a detector, column supplies, recorder, gases, and syringes. A data system capable of determining peak areas and integrating DRO as defined in the method is required.

6.1.2 Columns:

6.1.2.1 Column 1: 25 M x 0.25 mm Quadrex 007 5% methyl phenyl 0.5 micron film thickness.

6.1.2.2 Alternate Column: 30 M x 0.53 mm ID Restek RTX-5, 1.5 micron film thickness.

6.1.2.3 Other capillary columns may be used provided they are capable of resolving typical diesel components, and the solvent front from C₁₀.

6.1.2.4 Preference should be given to columns with low bleed characteristics.

6.1.3 Detector: Flame ionization (FID).

6.2 Concentrator tube. Kuderna-Danish - 10 ml graduated (Kontes K-570050-1025 or equivalent). Ground glass stopper is used to prevent evaporation of extracts.

6.3 Evaporative flask, Kuderna-Danish - Attach to concentrator tube with springs.

6.4 Snyder column, Kuderna-Danish - A rotary evaporator may also be used.

6.5 Nitrogen evaporator with high purity nitrogen gas source.

6.6 Analytical balance: A balance capable of accurately weighing 0.0001 g (must be used for standards). A top-loading balance capable of weighing to the nearest 0.1 g (should be used for sample analysis).

6.7 Ultrasonic bath.

- 6.8 Water bath - Heated with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.
- 6.9 VOC Vials and Bottles: Wide mouth 60 ml (2.0 oz.), or 120 ml (4.0 oz.) VOC vials with teflon/silicone septa or teflon lined caps for soils. Amber 1 liter bottles with teflon lined caps for waters.
- 6.10 Separatory funnel - 2000 ml with Teflon stopcock.
- 6.11 Microsyringes: 1 ul, 5 ul, 10 ul, 25 ul, and 100 ul.
- 6.12 Disposable pipets: Pasteur.
- 6.13 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).
- 7. Reagents and Standards
 - 7.1 Reagent Water: DRO free water
 - 7.2 Solvents: hexane, methylene chloride, carbon disulfide - pesticide grade or equivalent. Store away from other solvents. Note: Hexane is the recommended solvent for this method.
 - 7.3 DRO free Sodium sulfate - (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
 - 7.4 DRO free Sodium Chloride - (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
 - 7.5 DRO free sand or soil
 - 7.6 Surrogates are not mandatory in this method. However, if the laboratory intends to use surrogates, they must be chosen so that they do not elute within the DRO retention time window. Surrogates known to meet this criteria are Nonane (C_9) and Nonacosane (C_{29}).
 - 7.7 Individual Component Stock Standards: Volumetrically prepare individual stock standards for the diesel components in a solvent listed in 7.2 at approximately 20 mg/ml. (Some of the n-alkanes are available in solution in chloroform from Supelco Cat. #4-7102M and 4-7103M.)

- 7.7.1 Place about 8 mls of solvent in a 10 ml tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all solvent-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.
- 7.7.2 Using a 100 ul syringe, immediately add 20-30 ul of the diesel component to the flask; then reweigh. The liquid must fall directly into the solvent without contacting the neck of the flask.
- 7.7.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (ug/ul) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
- 7.7.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.
- 7.7.5 Standards must be replaced after six months unless comparison with unexpired standards documents their accuracy.
- 7.8 Diesel Component Stock Standard: Commercially prepared diesel component stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Diesel Component Stock Standards can be prepared using individual component stock standard solutions. Prepare Diesel Component Standard in a solvent listed in 7.2, as needed, at the concentrations shown in Table 3. These standards must be stored with minimal headspace and must be checked frequently for signs of degradation or evaporation.
- 7.9 Calibration Standards: Prepare Calibration standards at a minimum of five concentration levels in solvent from the Diesel Component Stock Standard. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC.

8. Sample collection, Preservation, and Handling

8.1 Aqueous samples should be collected in a one liter amber bottle with a teflon lined cap. The Teflon liner must contact the sample. Samples must be preserved with 5 mls of 50% HCl at the time of collection, (acid must be added to the bottle prior to adding the sample). Cool samples to 4°C immediately after collection. Water samples must be held at 4°C and extracted within seven days of collection. Analysis must take place within 47 days of collection. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples preserved with sodium azide or extracted within 48 hours of collection.

8.2 Soils can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore™ sampler or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1. A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination. Care must be taken to be sure the vial seals properly (no soil on the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

8.2.1 Collect and preserve samples by one of the following techniques:

8.2.1.1 Collect soil into tared VOC vials following Table 1. Store samples on ice or at 4°C. Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.

8.2.1.2 Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with teflon sheets placed between the endcaps and the sample. Store samples on ice or at 4°C. Immediately prior to solvent addition, the soil from the brass tube must be subsampled into a VOC vial following Table 1.

Subsampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

- 8.2.1.3 Pack soil with no headspace into an EnCore™ sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 4°C. Soil stored in the EnCore™ sampler must be extruded from the device into a VOC vial immediately prior to solvent addition. The soil is extruded by using a pushrod supplied with the tool. Soil should not be scooped out of the sampler using a spatula, etc. EnCore™ samplers must be cleaned appropriately (following the manufacturers recommendations) prior to reuse.
- 8.2.1.4 Alternate sample storage devices equivalent or superior in performance to the brass tube or the EnCore™ sampler may be used for sample storage prior to preservation in the laboratory. Alternate sample storage devices **must be approved** by the Department **prior to use**.
- 8.2.2 Shipping time should be minimized. Samples must be received by the lab within 72 hours. Refer to Table 2 for soil sample holding times.
 - 8.2.2.1 Extractant solvent must be added to soil vials within 72 hours of sample collection.
 - 8.2.2.2 Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 to determine the volume of solvent to add, or if the sample must be flagged or rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, at the request of clients, the samples must not be reported as "DRO".
 - 8.2.2.3 Add solvent to the sample in a 1:1 ratio (or greater) of mls solvent to grams of sample. Solvent can be injected through the septa, or the vial may be quickly opened to allow the appropriate volume of solvent to poured in. **Solvent must be added to the sample within 72 hours of sample collection.**
 - 8.2.2.4 It is not necessary for the lab to complete the extraction at the time of injection of the solvent (addition of sodium sulfate,

sonication, etc.) The date of solvent addition must be reported in lieu of the extraction date. Completion of the extraction (addition of sodium sulfate, sonication, etc.) need not be done until the time of analysis. Analysis must take place within 47 days of collection.

- 8.3 Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice". If samples are not "received on ice", temperature shall be determined from:

8.3.0.1 The temperature of an actual sample.

8.3.0.2 The temperature of a temperature blank shipped with samples.

8.3.0.3 The temperature of the melt water in the shipping container.

When no ice is in the cooler, no temperature blank is provided, and there is not sufficient sample volume to sacrifice for a temperature measurement, the laboratory must flag the sample result and state the condition of sample upon receipt (ie. not cooled during shipping, received at room temperature, etc.). **Note: If blue ice packs or similar methods are used, precooling of samples to 4°C with ice or by refrigeration is required.**

9. Procedure

- 9.1 Samples are analyzed by GC/FID. Waters are extracted using a separatory funnel or continuous liquid liquid extraction technique. Soils are extracted in the vial. Details are given in section 9.5. After the extracts are concentrated, a volume is injected directly onto the GC. The same solvent used for extraction must be used for calibration and analysis. Soil concentrations must be reported on a dry weight basis. The procedure for determination of dry weight can be found in EPA method 5030, section 7.3.3.1.5.

9.2 Gas Chromatography

- 9.2.1 Conditions: Set column temperature to 60°C for 2 minutes, then 12°C/min. to 320°C and hold for 15 min. (run time = 36 minutes). Set FID Detector to 320°C and injector to 280°C. Conditions may be altered to improve resolution of diesel range organics.
- 9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.3.

9.3 Retention Time Window and Quantitation

- 9.3.1 The retention time window is defined as beginning approximately 0.1 minutes before the onset of the n-decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.
- 9.3.2 Diesel Range Organics (DRO): Quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Diesel Component Standard. Further instructions on quantitation can be found in section 9.6.
- 9.3.3 The laboratory must verify the placement of the retention time window at the beginning of each day and whenever a new GC column is installed or when significant retention time shifts occur. This can be accomplished as part of the calibration check.
- 9.3.4 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. The correct baseline placement would be a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 is intended to illustrate correct placement of the baseline for several situations.

9.4 DRO Calibration

- 9.4.1 Run the Diesel Component Standard at a minimum of five concentration levels. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC.

- 9.4.2 Inject each calibration standard. A constant volume of extract must be injected for both samples and standards. Tabulate the entire area (baseline to baseline) for the ten components against the mass injected. Instructions on baseline to baseline integration can be found in section 9.6. The results are used to prepare a calibration curve by linear regression. The curve must have a correlation coefficient of at least 0.99.
 - 9.4.3 Verify the working calibration curve at the beginning of each working day, by the injection of a Calibration Check Standard (CCS). If the concentration determined from the curve, for the CCS, varies from the known concentration by more than 20%, attempt to correct the problem. If a CCS, run after corrective action has been performed, varies by more than 20% from the known concentration, a new calibration curve must be prepared.
- 9.5 Sample preparation
- 9.5.1 Water extraction - Separatory Funnel
 - 9.5.1.1 Check and note the initial pH. If the sample bottles had been supplied by the lab with acid for preservation then this is not required. However, it must be noted somewhere in the report (preferably on the Chain of Custody) that the bottles were supplied this way in lieu of a pH measurement. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifer samples preserved with sodium azide or extracted within 48 hours of collection.
 - 9.5.1.2 Measure a 1-L portion of the sample with a graduated cylinder and transfer to the 2-L separatory funnel. Record the volume. If the sample is in a 1 liter or smaller bottle, the analyst may measure the volume by marking the water meniscus on the side of the sample bottle for later determination. Determine the volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. For blanks and quality control standards, pour 1 liter of reagent water into the separatory funnel.
 - 9.5.1.3 Add 60 mls solvent to the sample bottle to rinse the inner walls (same solvent used for the calibration standards). If a graduated cylinder was used for volume measurement, this must

also be rinsed with solvent. Transfer the solvent to the separatory funnel. Add 100 g NaCl to separatory funnel. Extract the sample by shaking it for two minutes with frequent venting to release excess pressure.

- 9.5.1.4 Allow the layers to separate. Use mechanical techniques to break emulsions if they occur. Mechanical techniques include stirring, filtration through glass wool, and centrifugation.
- 9.5.1.5 Drain the solvent layer into a 250 ml beaker. If hexane is used for extraction the solvent layer will be on the top.
- 9.5.1.6 Repeat the extraction once more using a 60 ml aliquot of solvent. Collect the solvent in the same beaker described in 9.5.1.5.
- 9.5.1.7 Dry extract with Na_2SO_4 and add to Kuderna-Danish (K-D) evaporative concentrator. (The drying step need not be repeated for soil extracts.) Rinse the beaker and the Na_2SO_4 with small amounts of solvent. Add these rinses to the K-D.

NOTE: Equivalent concentration apparatus may be used.

- 9.5.1.8 Add a boiling chip to the K-D and attach a Snyder to the top. Pre-wet the column by adding about 1 ml of solvent to the top.

NOTE: The concentration step is critical; losses can occur if care is not taken.

- 9.5.1.9 Place the K-D in a heated water bath set at a temperature appropriate for the chosen solvent so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. When the appropriate volume has been reached, remove the K-D from the bath and allow it to cool completely.
- 9.5.1.10 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of solvent. Transfer the extract to a calibrated 15 ml centrifuge tube, rinsing with a small amount of

solvent. Be sure to rinse all of the ground glass joints well, as compounds collect on the ground glass.

- 9.5.1.11 Carefully concentrate the extract to 1.0 ml under a gentle stream of nitrogen. The final volume can be greater than 1.0 ml as long as the laboratory can meet the method LOQ. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. Transfer to an appropriate sized vial with Teflon lined cap, mark the meniscus for final extract volume determination.
 - 9.5.1.12 Record the preparation information for the extraction and concentration steps. The sample extract is ready for analysis in section 9.5.4.
- 9.5.2 Water extraction - Continuous liquid liquid extraction
- 9.5.2.1 Mount the continuous extractor on appropriate racks.
 - 9.5.2.2 Put 250 ml solvent in a round bottom flask, add a few boiling chips (same solvent used for the calibration standards). Add 300 ml of solvent to the extractor flask.
 - 9.5.2.3 When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water into either sidearm by pouring the water down the back of the extractor.
 - 9.5.2.4 Check and note the pH. If the sample bottles had been supplied by the lab with acid for preservation then this is not required. However, it should be noted somewhere in the report (preferably on the Chain of Custody) that the bottles were supplied this way in lieu of a pH measurement. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifer samples preserved with sodium azide or extracted within 48 hours of collection.
 - 9.5.2.5 Measure a 1-L portion of the sample with a graduated cylinder and transfer into the extractor flask. Record the volume. If the sample is in a 1 liter or smaller bottle, the analyst may measure the volume by marking the water meniscus on the side of the

sample bottle for later determination. Determine the volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. Pour the sample into the extractor flask. For blanks and quality control standards, pour 1 liter of reagent water into the separatory funnel.

- 9.5.2.6 Add enough reagent water to the extractor flask to allow the solvent in the removable sidearm to just begin to drip into the round bottom flask. Record the total volume of reagent water that was added on the prep sheet.
 - 9.5.2.7 Remove the condenser from the rack and wipe the lower joint and lip with a tissue soaked with solvent. Place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators.
 - 9.5.2.8 Turn on the heating mantle. Check after 15 minutes to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip on the condenser, and that the volume of the solvent in the round bottom flask is still about 240 ml.
 - 9.5.2.9 Check all extractor joints for leaks with a Kimwipe. Allow the extraction to proceed for 18-24 hours.
 - 9.5.2.10 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.
 - 9.5.2.11 The solvent contained in the round bottom flask is the extract. Transfer the extract to a 400 ml beaker, rinsing with a small amount of solvent. If the volume of solvent is less than about 250 ml, record the solvent volume.
 - 9.5.2.12 Go to 9.5.1.7 and proceed with the prep.
- 9.5.3 Solvent Extraction for Soil/Sediment: This method is based on extracting the sediment/soil with solvent. An aliquot of the extract is concentrated and injected on the GC.

- 9.5.3.1 Add 25 gms of dried Na_2SO_4 to sample preserved in section 8.2.2.
- 9.5.3.2 Hand shake sample in its vial vigorously for 2 minutes. Sonicate for 20 minutes. If the sample is not well mixed then stir the mixture with a steel spatula, shake for 2 minutes and resonicate.
- 9.5.3.3 Allow sediment to settle until a layer of solvent is apparent.
- 9.5.3.4 Decant the solvent or remove with a syringe into a 150 ml beaker.
- 9.5.3.5 Repeat extraction once more and combine the extracts.
- 9.5.3.6 Go to 9.5.1.7 and proceed with the prep.
- 9.5.4 Inject an appropriate volume of concentrated extract onto the GC and proceed with the analysis. A constant volume of extract must be injected for both samples and standards. If the sample response exceeds the calibration range for the DRO an appropriate dilution should be used. An appropriate dilution is one that keeps the response (both area and peak height) of major constituents in the upper half of the calibration range. If an initial dilution does not accomplish this then an intermediate dilution should be performed.

9.6 Calculations:

- 9.6.1 DRO Calibration: Quantitation of DRO is performed by the external standard method. The concentration of Diesel Range Organics in the sample is determined from a summation of the total response within the range of the elution of n-decane and n-octacosane, using the calibration curve. No area may be subtracted from the DRO retention time window in calculating DRO results.
 - 9.6.1.1 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The correct baseline coincides with a horizontal line drawn through the lowest point in the chromatogram before the end of the

window. The lowest point may be within the window, before the window, or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 illustrates correct placement of the baseline for several chromatograms.

- 9.6.1.2 Refer to Section 9.3, Retention Time Windows and Quantitation, for information on establishing the retention time window. From linear regression of calibration standard GC responses (R) against their known concentrations (C in ug/ml) derive the following linear equation:

$$C = mR + b$$

Using the slope (m) and the intercept (b) from this equation the concentration of the sample can be calculated from the following equations:

Water samples

$$C_s = [(mR_s + b)(V_E)(D)]/V_s$$

Soil Samples

$$C_s = [(mR_s + b)(V_E)(D)]/W$$

Where:

C_s = Concentration of sample in ug/l for waters and mg/kg on a dry weight basis for soils

m = slope of the calibration curve

R_s = GC response of sample in the DRO retention time window

b = intercept of calibration curve

V_E = total volume of sample extract (after concentration) in ml

V_s = volume of water sample in liters

D = dilution factor if extract was diluted

W = total dry weight of soil sample in gm

- 9.6.2 Peak areas measured from blanks may not be subtracted from sample peak areas. All blank concentrations (above the LOD) must be reported. Sections 10.3.3 and 10.3.4 give acceptance criteria for blanks. Blank concentrations up to and including the acceptance criteria must be reported. Blank concentrations exceeding the acceptance criteria require reanalysis.
- 9.6.3 Report the presence of significant peaks outside the chromatographic window. Significant peaks are peaks which can be distinguished above the noise in a chromatogram. Any peak 3 times the standard deviation of the signal to noise ratio is statistically significant. To accommodate heavier oils and to insure that peaks outside the DRO window are not missed, run the chromatogram out 5 minutes past the last component in the DRO component standard. All peaks (and baseline rises) outside the window are to be reported. If area outside the window is detected it must not be quantitated as part of the DRO result. Laboratories may quantitate this area outside the window against the DRO standard and report a concentration detected outside the window or simply report that peaks or baseline rises were detected outside the window.
- 9.6.4 All area detected in the DRO window must be reported as "DRO". Reporting "nonpattern match", "nonapplicable", "nonpetroleum" etc. will not be acceptable. If the Consultant or RP feel that the DRO result does not represent contamination at the site, for example, if they wish to attribute the DRO detection to naturally occurring organics then confirmation by mass spectroscopy will be required. For further information on MS confirmation see the "LUST and Petroleum Analytical and Quality Assurance Guidance", #PUBL-SW-130, most recent revision, (Section 8.0, Soil Analytes Table, footnotes).

10. Quality Control

- 10.1 The analyst must make an initial demonstration of the capability to generate acceptable accuracy and precision with this method by successful analysis of the following:
- 10.1.1 Replicate Laboratory Control Spike - Water: Analysis of 5 replicates at a concentration of 100 ug/l. Recoveries must fall between 75%-115% of the known concentration and the RSD must be <20%.
- 10.1.2 Replicate Laboratory Control Spike - Soil: Analysis of 5 replicates at a concentration of 10 mg/kg. Recoveries must fall between 70%-120% of the known concentration and the RSD must be <20%.
- 10.2 The laboratory must determine its LOD and LOQ for both soils and waters. The LOD determination must be performed in accordance with 40 CFR, Part 136, Appendix B. Soil LODs are performed in accordance with 40 CFR, Part 136, Appendix B using a DRO free sand or soil, and the same extraction method used for soil samples. The LOQ calculation can be found in "Principles of Environmental Analysis", Analytical Chemistry, Vol. 55, No. 14, December 1983, 2210-2218. The LOQ is defined as:

$$LOQ = 10(S)$$

Where S is the standard deviation determined from analysis of seven replicate spikes analyzed to determine the LOD in accordance with 40 CFR, Part 136, Appendix B.

- 10.3 With every batch of 20 samples or less the lab must analyze:
- 10.3.1 Duplicate Laboratory Control Spike - Water : The Duplicate LCS-water must be processed through the method in the same manner as water samples. The recovery of the LCS-water spikes must be between 75%-115% and the RPD<20%. The LCS-water must be run with every batch of 20 water samples. One of the LCS-waters must be run at the beginning of a batch of samples and the other at the end.
- Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS

run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

- 10.3.2 Duplicate Laboratory Control Spike - Soil : The Duplicate LCS-soil must be run through the method in the same manner as soil samples. The recovery of the LCS-soil spikes must be between 70%-120% and the RPD<20%. The LCS-soil must be run with every batch of 20 soil samples. One of the LCS-soils must be run at the beginning of a batch of samples and the other at the end.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

- 10.3.3 Method Blank - water: The method blank - water must be processed through the method in the same manner as water samples. If the concentration exceeds 50 ug/l, all water samples associated with this blank (samples run since the last blank that was below 50 ug/l) must be rerun.
- 10.3.4 Method Blank - soil: The method blank - soil must be processed through the method in the same manner as soil samples. If the concentration exceeds 5.0 mg/kg, all soil samples associated with this blank (samples run since the last blank that was below 5.0 mg/kg) must be rerun.
- 10.3.5 Calibration Check Standard (CCS): The CCS response must be within \pm 20% of the value predicted by the curve or a new curve must be generated. The CCS must not be used to update the curve or used in any other manner for quantitation.

- 10.4 The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99.
- 10.5 If any of the criteria above are not met, the problem must be corrected before further samples are analyzed. Any samples analyzed between the last QC samples that meet the criteria and those that have fallen out must be rerun. If this is not possible, affected sample results must be flagged.
- 10.6 Solvent blanks should be run after samples suspected of being highly concentrated to prevent carryover.

10.7 Standard diesel fuel and other heavy end fuel mixtures are available commercially if the laboratory desires additional performance indicators.

11. Method Performance

11.1 The required Limit of Quantitation (LOQ) is 10 mg/kg or less for soils and 0.1 mg/l or less for waters. A chromatogram for the Diesel Component Standard is in Figure 2.

12. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 8000, 8100, 3510, 3520, 3540, and 3550.
2. "Method OA-2: Extractable Petroleum in Products", Revision January 10, 1990; University Hygienic Laboratory, Iowa City, Iowa.
3. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water" - Draft - February 28, 1990; prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.
4. Silis, K., M. McDevitt, and J. Parr; "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment", presented at the conference on Petroleum Hydrocarbons and organic Chemicals in Groundwater, NWWA, Houston, Texas, November 1988.
5. "Leaking Underground Fuel Tank (LUFT) Field Manual", State Water Resources Control Board, State of California, Sacramento, CA, May 1988.
6. Fitzgerald, John; "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure", Petroleum Contaminated Soils, Vol. 2, 1989.
7. Senn, R.B., and M.S. Johnson; "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigation", Ground Water Monitoring Review, 1987.
8. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" presented at 5th Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989.
9. ASTM "Standards Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," 3328-78.

Wisconsin DNR Modified DRO Method
September 1995

Table 1
Weight Maxima

Vial Size	Target Sample Weight	Actual Sample Weight	Minimum Volume of Solvent	Action
60 mls	25 gms	<25 gms	25 mls	Adjust MDL
		25-35 gms	≥25-35 mls	Add Solvent
		>35 gms	for any amount	Reject
120 mls	25 gms or 50 gms	<25 gms	25 mls	Adjust MDL
		25-70 gms	≥25-70 mls	Add Solvent
		>70 gms	for any amount	Reject

Laboratories should use standard rounding rules to determine compliance with the maximum weight requirement. Sample weights should be rounded to the nearest whole number. This means that a sample weighing between 34.5-35.4 is rounded to 35.0 gms, and a sample weighing between 69.5-70.4 gms is rounded to 70.0 gms. There will be NO allowances given past these tolerances.

Table 2
Sample Holding Times and Storage

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		Solvent Addition	Shipping	Extraction	Analysis
DRO waters	Amber Bottle	NA	7 days	7 days	47 days
DRO carbonate aquifers	Amber Bottle	NA	2 days unless azide preserved	2 days unless azide preserved	47 days
DRO soils	VOC vial	within 72 hours	72 hours	47 days	47 days
	Brass Tube or EnCore™	within 72 hours	72 hours	47 days	47 days

Table 3

DIESEL COMPONENT STANDARD AND CONCENTRATIONS	
Component	Concentration, ug/ml
Decane	1000
Dodecane	1000
Tetradecane	1000
Hexadecane	1000
Octadecane	1000
Eicosane	1000
Docosane	1000
Tetracosane	1000
Hexacosane	1000
Octacosane	1000
Total	10,000

Note: The concentration of the Diesel Component Standard may be varied as long as the concentration of each component is the same.

Figure 1
Integration Examples

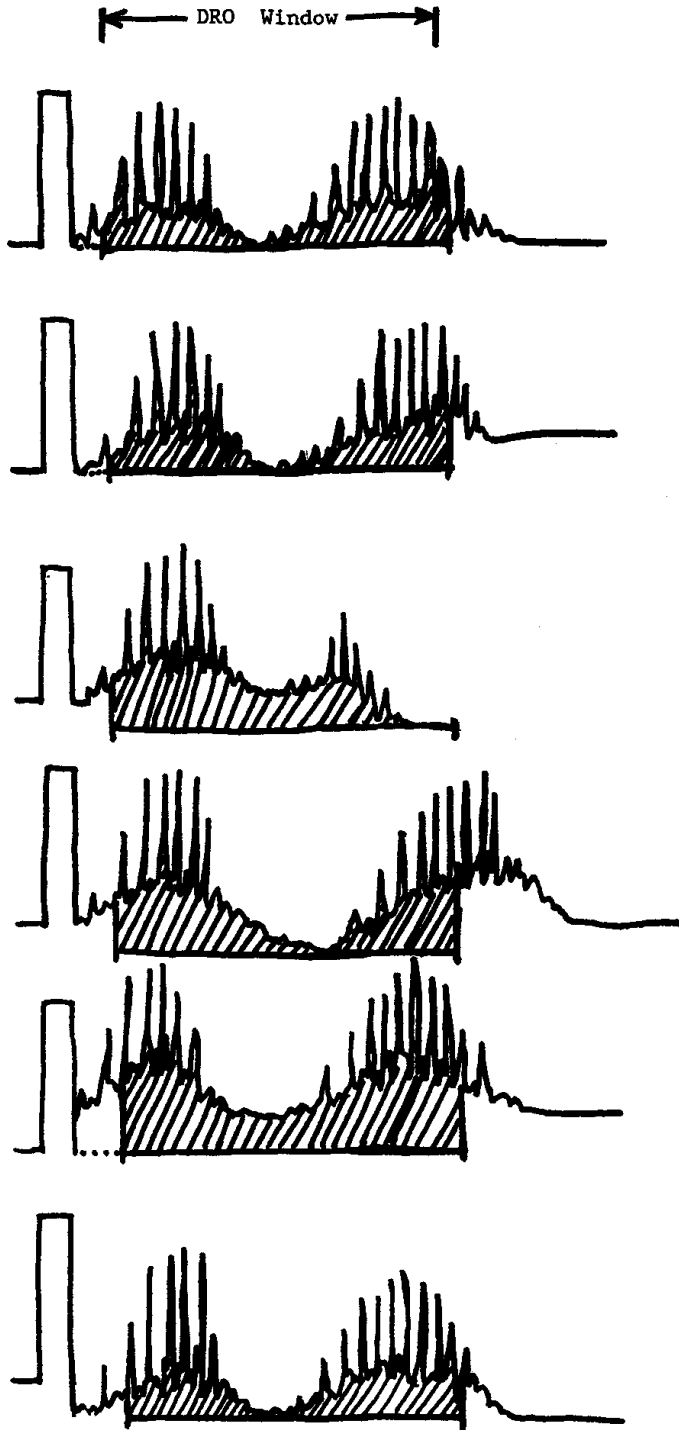


FIGURE 2
Diesel Component Standard

